FRACTAL DIMENSION ANALYSIS OF CHARS PRODUCED FROM SYNTHETIC COAL

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ABSTRACT

The fractal dimension, a measure of surface ruggedness, of chars was measured using physisorption techniques. Coals and chars at different stages of combustion were prepared in a laminar flow (drop-tube) furnace. By adjusting the residence time of the coal and char particles in the drop tube, the particles experienced combustion conditions for various lengths of time. The particles were quickly cooled and quenched in an inert atmosphere. The samples were analyzed using a scanning electron microprobe and by using the physisorption of a series of gases. The adsorption data was used to test if the char surface was fractal and to determine the fractal dimension. Changes in the fractal dimension during combustion were quantified. As the char was burned the fractal dimension increased as the carbon matrix burned away leaving mineral moieties. As combustion continued and the carbon burned completely away leaving a mineral fly ash particle the fractal dimension decreased again. Fractal dimension information will be used to model the formation of surface moieties that occur on the char from the inorganic mineral matter dispersed within the coal (Benson *et.al.*, 1988).

BACKGROUND

The morphology and adsorption characteristics of a char surface affect the rate of combustion and the mass transfer processes of the reactants and products involved. A recently developed experimental technique, fractal analysis using physisorption, was used to measure the development of surface morphology during combustion. The conditions at the surface of a burning coal or char particle affect the rate of combustion and the extent of conversion which, in turn, affects the formation of combustion products and unwanted by-products. A laminar flow (drop-tube) furnace was used to produce chars at various stages of combustion for this study.

Background: Physical Adsorption and Surface Area

The adsorption of gases on porous solids is used to measure the surface area of the solid by determining the amount of gas adsorbed as a function of the partial pressure of the adsorbate. Standard surface area determinations are made by adsorbing nitrogen at 77 K and calculating the surface area using the model developed by Brunauer, Emmett and Teller (1938), known as BET (Gregg and Sing, 1982). Other adsorption models can be used. The adsorption model of Dubinin-Polanyi (DP) has been used to determine the surface area of coals and chars(Gregg and Sing, 1982; Marsh and Siemieniewska, 1965). For this research the BET model gave better correlation of the adsorption data (higher correlation coefficients) and was used for all gases. The dynamic flow system was used to determine the gas adsorption isotherms for this research and will be described in the "methods" section.

Background: Fractal Analysis

Adsorption of gases other than nitrogen have been successfully used to measure surface area. Each adsorbing gas has a different molecular size and the surface area covered by an adsorbed molecule of several gases has been determined (Gregg and Sing, 1982, McClellan and Harnsberger, 1967). Mathematical strategies for describing rugged or indeterminate boundaries, known as fractal geometry, developed by Mandelbrot (1977, 1982) have recently been applied to the description of surface structure (Avnir, 1986, 1989; Avnir and Pfeifer, 1983; Avnir *et.al.*, 1983, 1984, 1985; Delfosse *et.al.*, 1988; Fairbridge *et.al.*, 1986; Farin *et.al.*, 1984, 1985a, 1985b; Fripiat *et.al.*, 1986; Jabkhiro and Delfosse, 1988; Ludlow and Moberg, 1990; McEnaney 1988; Moberg, 1990; Ng *et.al.*, 1987; Pfeifer, 1984; Pfeifer and Avnir, 1983; Pfeifer *et.al.*, 1983, 1984; Van Damme and Fripiat, 1985; Van Vliet and Young, 1988; Vosen, 1990; Wilkie, 1990). Theories have been developed to determine a quantity known as the "fractal dimension," which is a measure of the ruggedness of a surface. The value of the fractal dimension varies from the topological dimension of 2 to the euclidean dimension of 3. When a molecule interacts with a surface having a fractal dimension of 2.0 it is essentially encountering a two dimensional plane. When the fractal dimension approaches 3.0, an adsorbing molecule is encountering a three dimensional surface.

Two methods to determine the fractal dimension of solids from adsorption data have been demonstrated. In the first method a single adsorbate is used, and the surface area is measured using different particle sizes of the sample. This technique requires grinding the sample, using a sonic sieve to size the particles into very tight particle ranges, and measuring particle size distribution in each range. This method has been demonstrated (Avnir *et.al.*, 1985; Fairbridge *et.al.*, 1986; Ng *et.al.*, 1987) and has the major advantage that only one adsorbate is required. The disadvantages are the extensive sample preparation required and the possibility that grinding the sample may affect the fractal dimension.

The second method to determine fractal dimension is to adsorb a series of different sized molecules onto a single sample. Because the smaller molecules have access to the "finer" surface structure that the larger molecules do not, a difference in measured surface area is found. Using this difference, a scheme has been developed to determine the fractal dimension. This method has also been demonstrated (Avnir *et.al.*, 1985; Van Damme and Fripiat, 1985). The second method does not explicitly require the sonic sieve, nor the particle size analyzer, but it does require the ability to adsorb different gases onto the sample. Using a mass flow controller and a gas handling manifold, various adsorbate/helium mixtures can be used for surface analysis.

Background: Inorganics in Coal

One objective of this study is to determine the effect that temperature and residence times, found in typical industrial pulverized-coal boilers, have on the formation of char and fly ash morphology. Sodium silicates and sodium sulfates form the major inorganic constituents of coal. These inorganic constituents will affect the surface structure of the chars and fly ash being developed. Western coals contain significant quantities of sodium, sulfur, and silica. The inorganic constituents of coal pass through the combustion zone either as solids, liquids or vapor and ultimately react or condense to form fly ash particles. Some of the fly ash particles are transported to the heat exchange surfaces and form a deposit which will grow with time. As these deposits increase they insulate the heat transfer surface, decreasing the thermal efficiency of the boiler.

Sodium volatilizes upon combustion, becomes dispersed through the gas stream, and later condenses on other ash particles and on the metal surfaces. Wibberly and Wall(1982) proposed that sodium containing materials provide a binding matrix that fuses ash particles together. The mechanism of formation of such a material may be the key to understanding the deposition processes of western coals. Studies by Sondreal(1977) on low rank coals from the western U.S. revealed that the severity of ash fouling deposits correlates not only with sodium concentration but also with total ash content.

One of the major problems in studying the roles of inorganics during coal combustion is the complexity of coal. To alleviate this problem, the interaction of the three inorganic constituents were studied in a model system with use of a synthetic coal (glassy carbon) incorporated with the desired inorganics(Erickson 1988; Erickson 1990).

EXPERIMENTAL METHODS

Synthetic Coal Preparation

The purpose of a synthetic coal is to be able to study the interactions of coal combustion in a system not as complex as actual coal. The synthetic coal must have similar combustion characteristics as well as lending itself to the addition of minerals in a quantitative manner. A furfuryl alcohol polymer has been found to be such a substance(Schmitt 1976; Senior and Flagen 1984; Levendis and Flagen 1987).

The preparation of the synthetic coal was developed by Senior(1984). The technique was slightly modified for this study and is described in detail(Erickson 1990). In brief, the quartz (which had been sized to 5 mm) was added prior to the polymerization so that it would behave as an included mineral. After the polymer was cured, the synthetic coal was ground and sized. Analysis of the sized coal indicated that 0.4 weight percent sulfur was inherent in the synthetic coal polymer due to the p-toluensulfonic acid which is used as a catalyst for the polymerization. Additional sublimed sulfur was added extraneously and mixed with the ground synthetic coal so that the final composition would consist of 1% sulfur. Sodium was added using a solution of sodium benzoate in an ethanol solution. The sodium benzoate/alcohol solution was mixed with the ground coal and the alcohol evaporated. This has been found(Mills 1989) to effectively load the sodium on the coal so that it will easily volatilize.

The chemistry of the polymerization of furfuryl alcohol to form a glassy carbon has been studied extensively(Dunlop and Peters 1953; Riesz and Susman 1960; Conley and Metil 1963; Weswerka et.al 1968; Fitzer et.al 1969). For this study characterization of the synthetic coal included analysis by SEM, CCSEM, TGA, Proximate-Ultimate, Inductively Coupled Plasma (ICP) (with acid digestion and lithium boride extraction), BET surface area from nitrogen adsorption and fractal analysis using gas adsorption. By formulation and analysis the synthetic coal included 10 percent SiO_2 (quartz), 5 percent Na and 1 percent S by weight. The weight loss with respect to temperature from the TGA were in qualitative agreement with TGA results for a low rank coal. The nitrogen BET surface area of the synthetic coal is 50.3 m^2 /g.

Laminar Flow Furnace

The prepared samples of synthetic coal were burned in the laminar flow furnace with 20 percent excess air (to ensure complete combustion). The laminar flow furnace is an instrument available through the University of North Dakota, Energy and Environmental Research Center(Zygarlicke *et.al.*, 1989). The pulverized and sized synthetic coal is fed to the laminar flow furnace and burned under preset conditions. The char and fly ash is collected using a water-cooled, nitrogen-quenched probe and collected on filter paper. Six different samples of char and fly ash were prepared using the laminar flow furnace. These six samples along with two samples of synthetic coal were analyzed using the scanning electron microprobe and fractal dimension analysis.

Gas Adsorption

A dynamic flow adsorption instrument is one of the most popular methods to measure gas adsorption. A mixture of adsorbate and helium passes through a thermal conductivity (TC) detector, across the sample, and then through a matched TC detector. The TC detectors are connected in a bridge circuit so that a millivolt signal, which is

proportional to the difference in the concentrations of the adsorbate before and after flowing through the sample, is generated. When flow across the sample is initiated, a signal will be generated from the bridged TC detectors because the concentration of the adsorbate will decrease as it is adsorbed onto the surface. A signal will not be generated by the TC detectors when equilibrium has been achieved. The amount adsorbed is determined from the area under the curve of a plot of the TC signal versus time. To accurately measure the surface area the amount adsorbed should be determined at three to five different adsorbate/helium compositions. However, due to experimental difficulty, some samples were analyzed at only two compositions.

A Micromeritics, Flowsorb 2300 II with a mass flow controller was used to obtain all gas adsorption measurements. The instrument was plumbed so that several different adsorbates (nitrogen, carbon dioxide, ethane, propane and n-butane) can be mixed with helium and used for gas adsorption.

To measure the complete isotherm, each adsorbate was adsorbed at different partial pressures. In order for physical adsorption to occur, the adsorption conditions need to be close to the boiling temperature of the adsorbate. Desorption temperatures are set at any convenient temperature above the adsorption temperature so that desorption will occur.

BET Equation

The BET adsorption model (Brunauer *et.al.*, 1938) is commonly used to determine surface area from physisorption data. The relation:

$$\frac{P}{V(P_o-P)} = \frac{1}{V_mC} + \frac{C-1}{V_mC}\frac{P}{P_o} \quad (1)$$

is used to determine V_m, the monolayer coverage. In the equation, P is the adsorbate partial pressure (mmHg), P_o is the saturation pressure (mmHg), and V is the volume adsorbed (cm^3 STP/g of sample). The constant C is an experimentally determined constant which is related to the heat of adsorption. The BET equation is considered valid for values of C between 10 and 110. For values of C between 2 and 10 the relationship can be applied but may be within 100% error. For C values greater than 110 the model is expected to be within 20% error. Using Equation 1 the monolayer coverage can be determined from the slope and intercept of a plot of $P/V(P_o-P)$ versus P/P_o.

Fractal Dimension Analysis

The concepts developed by Mandelbrot (1977, 1982) can be applied to the determination of surface ruggedness. Different sized molecules will have different access to surfaces that are rugged or indeterminate. This concept can be visualized in Figure 1. Avnir (1989) developed the relationship:

$$V_m \propto \sigma^{(-D/2)} \quad (3)$$

where V_m is the monolayer coverage, σ is the cross-sectional area of the adsorbate molecule, and D is the fractal dimension. This equation can be written as:

$$V_m = k\sigma^{(-D/2)} \quad (4)$$

where k is a prefactor which contains the necessary dimensional conversions. This term is called the lacunarity (Mandelbrot, 1982). The constant k is the monolayer value for unit σ and carries information about the connectivity and porosity of the surface (larger values of k correspond to a greater extent of porosity). The value of D is expected to have a value between 2 and 3.

Equation 4 can be linearized by taking the logarithm of both sides, which results in:

$$\log V_m = \log k - D/2 \log\sigma \quad (5)$$

Equation 5 is the working relationship, and indicates that a plot of $\log V_m$ versus $\log\sigma$ for various adsorbates on a given adsorbent should be a straight line with slope of -D/2 and intercept of log k.

Experimental Matrix

In order to maintain the experimental integrity of the study and to eliminate any operator bias, the order in which the various adsorptions were performed was randomized. Five sample holders for the gas adsorption unit were available so a suite of five samples were run first followed by a suite of three samples. The order in which the adsorbates were used was randomized, the order in which the various gas compositions were used was randomized, and finally the order in which the samples were analyzed at each composition was randomized. For each adsorbate composition on a given sample, four to six adsorption/desorptions were performed.

RESULTS

The synthetic coal sample was prepared and burned in the laminar flow furnace. The resulting chars and fly ash particles were collected and characterized using the SEM, CCSEM and TGA. The remaining char and fly ash particles were used for the gas adsorption analyses. Figure 2 shows a typical BET plot (nitrogen on sample 3).

Using the gas adsorption data (V_m) and McClellan and Harnsberger's (1967) cross-sectional areas, fractal plots were made for each sample. A sample plot is shown in Figure 3. The fractal dimension determined for each sample is found in Table 1.

DISCUSSION OF RESULTS

As the synthetic coal particles burn the carbon matrix is removed and the remaining mineral constituents form small beads on the char surface. There is evidence of the interaction of the sodium with the silica because the mineral

particles have rounded edges corresponding to a sodium silicate particle. At the operating temperatures, silica is not expected to be molten. However, the heat released during the combustion, may be enough to raise the particle temperature to point above the melting point of silica.

The formation of the sodium silicate moieties on the surface of the char drastically changes the surface morphology of the chars at the different stages of combustion. This was evident in the SEM micrographs. The determination of the fractal dimensions gives a quantitative description of the surface ruggedness. For the synthetic coal particles the surface fractal dimension is initially close to 2. As the particle burns and there is an increase in the ruggedness and the fractal dimension increases. Finally as the carbon matrix completely burns away and the remaining minerals coalesce, the fractal dimension decreases. This is demonstrated in Figure 4 which shows the plot of fractal dimension versus carbon loss. The lacunarity (prefactor) also gives some information about the degree of connectivity and porosity of the surface. The lacunarity also increases in the initial stages of combustion and again decreases as the mineral matter starts to coalesce. This is shown in Figure 5.

Sample Size

The results for some of the samples are less than satisfactory. The primary difficulty with these samples was that there was not enough sample produced in the laminar flow furnace. The Flowsorb II 2300 has resolution down to 0.002 cm^3 STP, however, the accuracy falls off for adsorptions below 0.2 cm^3 STP. Typical procedures for samples with a total volume adsorbed less than 0.2 cm^3 STP is to load the sample cells with more sample. Due to the prohibitive cost of producing more char and fly ash samples, it was decided to attempt the analyses with the existing samples (samples 7 and 8) which were smaller than desired. It was evident from the results that the range of the instrumentation had been exceeded for the smaller sized samples.

Sample Analysis Time

A difficulty that may prevent fractal dimension analysis from becoming a "routine" analysis is the time involved in obtaining the adsorption data. For each sample, five different adsorbates were used, and each adsorbate was adsorbed at three to five different compositions. In addition, at each composition from four to six adsorption/desorption cycles were performed. Each adsorption/desorption cycle requires from one to one and a half hours to complete. Thus the analysis time to determine the fractal dimension of a single sample takes on the order of 100 hours of instrument (operator) time.

However, due to the quantitative nature of the resulting measure of surface ruggedness, the technique still has applications with selected samples of important research applications. There is the possibility that the technique can be further refined to decrease the total analysis time required for each sample.

Cross-sectional areas

An additional difficulty with the analysis is that of determining to correct cross-sectional area of the molecules. This is a notorious problem of surface science (Farin et.al., 1985; Meyer et.al. 1986; McClellan and Harnsberger, 1967) and has yet to receive satisfactory solution. The current state of knowledge is the predictions given by McClellan and Harnsberger (1967). The difficulty with these correlations is that the predictions are based on the idea that different adsorbates should give the same surface area. This can only be true if the adsorbent has a molecularly smooth surface with a fractal dimension of 2. Since McClellan and Harnsberger's work was completed before the concept of fractal surfaces appeared in the literature, these considerations were not taken into account.

CONCLUSIONS

The surface fractal dimension of burning synthetic coal at different stages of combustion have been determined (Vosen, 1990). The experimental technique of using dynamic flow adsorption instrument to determine fractal dimension from gas adsorption data has been demonstrated (Ludlow and Moberg, 1990; Moberg, 1990; Vosen, 1990; Wilkie, 1990). Information (experience) obtained from this study will lead to further improvements of the technique. The fractal dimensions determined, for samples with sufficient sample size, corresponded well with the apparent changes in surface structure at the different stages of combustion.

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TABLE 1
Results

Run	Combustion Temperature (K)	Residence Time (sec)	Sample Size (g)	Mineral[A] Diameter (mm)	Carbon[B] Loss (%)	BET Surface[C] Area (m^2/g)	Fractal Dimension D	Prefactor K (Å^D cm^3 STP)
1	Synthetic Coal	-	0.6319	3.84	0.0	49.0± 1.6	1.89± 0.49	9.35 ± 2.18
2	Synthetic Coal	-	0.6576	3.84	0.0	51.5± 1.4	2.10± 0.28	10.69± 2.10
3	1173	0.1	0.6142	4.04	14.3	55.1± 1.3	2.70± 0.83	16.05± 2.31
4	1173	0.5	0.1568	4.06	66.5	124.7± 3.3	2.85± 0.30	22.67± 2.11
5	1173	1.5	0.1816	27.0[E]	100	121.4± 3.1	2.47± 0.72	16.86± 2.26
6	1773	0.1	0.3089	5.06	48.7	110.4± 3.0	2.81± 0.46	21.79± 2.17
7	1773	0.5	0.0253	4.20	83.5	(5.6± 0.5)[F]	1.98± 1.15	3.26± 2.30
8	1773	1.5	0.3071	8.50[E]	100	(0.8± 0.1)[F]	2.26± 1.84	1.78± 2.48

[A] Determined using CCSEM
[B] Determined using TGA
[C] Nitrogen Adsorption data at 77 K
[E] Average diameter of coalesced fly ash particles
[F] Insufficient sample size to accurately determine surface area

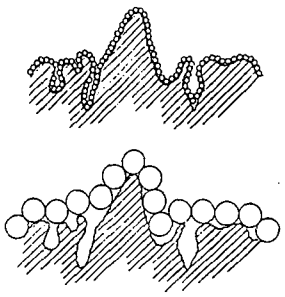

Figure 1. Pictorial representation of fractal dimension analysis.

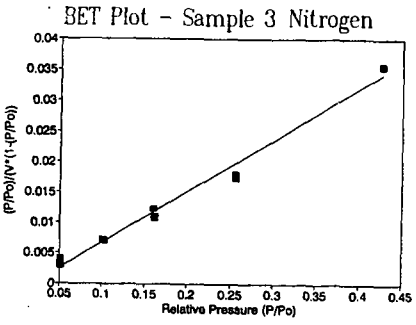

Figure 2. Example of BET plot used to determine monolayer volume adsorbed (V_m).

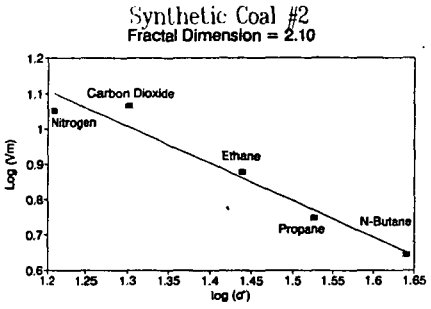

Figure 3. Example of fractal dimension plot used to determine the fractal dimension, D, and the lacunarity.

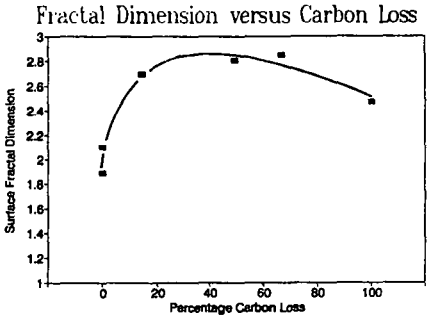

Figure 4. Surface fractal dimension versus carbon loss during char combustion.

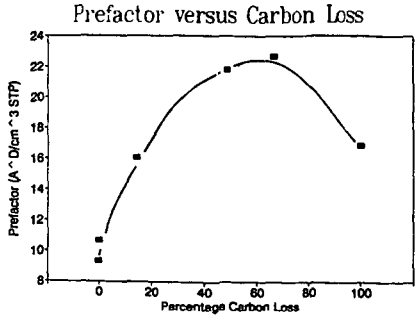

Figure 5. Lacunarity versus carbon loss during char combustion.